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Synthesis and Characterization of Carboxylate-FeOOH Nanoparticles (Ferroxanes) and Ferroxane-Derived Ceramics

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Scientists from the University of Aix-Marseille in France, Rice University in Houston, and the University of Georgia in Aiken have shown that the reaction between a natural iron mineral named lepidocrocite (γ -FeOOH) and acetic acid ($C_2H_4O_2$, denoted AA) in water results in the formation of carboxylate-FeOOH nanoparticles called ferroxane-AA. Upon thermolysis (cleavage of atomic bonds by exposure to high temperature), the nanoparticles evolve to homogeneous iron-metal oxides. A low firing temperature for conversion to ceramic as well as the use of environmentally benign reagents suggest that this process for creating ferroxane-derived ceramics should have minimal environmental impact.

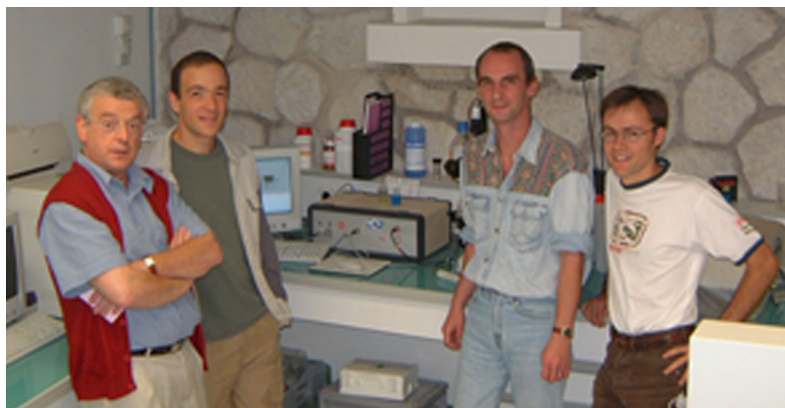
Ceramic oxides are widely used in industry (for example as catalysts, paint pigments, medical supplies, chemical sorbents, and magnetic products), so new synthetic methods to produce iron oxide are constantly developed. Two common processes are currently used to produce oxide ceramics: powder processing and sol-gel. But powder processing – which is typically used to produce bulk quantities of the ceramic – involves potentially toxic agents, such as binders and solvents, and the sol-gel process may yield environmentally harmful products such as strong acids, binders, and solvents.

It is thus desirable to develop new synthetic methodologies to overcome the drawbacks of current processing techniques. We have developed a new approach for the synthesis of iron oxide ceramics based upon the reaction of large minerals with carboxylic acids. A new iron precursor for iron-ceramics, called carboxylate-ferroxane (carboxylate-FeOOH), was prepared by reacting lepidocrocite (γ -FeOOH), a layered mineral, with acetic acid (AA) in water.

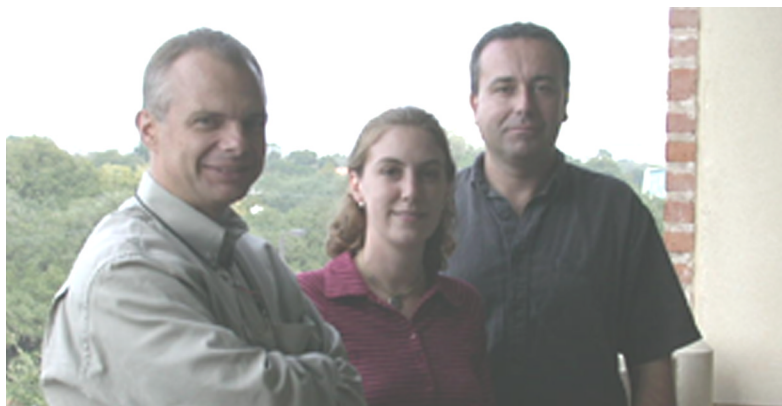
The atomic environment of iron within the ferroxane was determined using iron K-edge x-ray ab-

sorption spectroscopy (XAS) of the dehydrated samples. The

ferroxanes were also doped with zirconium, the structural site of



Members of the team at the University of Aix-Marseille in France (from left to right): Jean-Yves Bottero, Stéphane Moustier, Armand Masion, and Jérôme Rose (lead author).



Members of the Rice University team (from left to right): Mark Wiesner, Maria Cortalezzi, and Andrew Barron.

which was characterized at the zirconium K-edge. XAS spectra were recorded at NSLS beamline X23A2.

The structure and texture of the ferroxane were characterized by combining spectroscopic methods (Fourier-Transform Infrared (FTIR), XAS, x-ray diffraction (XRD), and light scattering), microscopic methods (atomic force microscopy (AFM) and scanning electron microscopy (SEM)) and gas adsorption data.

The current results (**Figure 1**) show that AA may cleave and break the lepidocrocite, yielding a new product: ferroxane. Ferroxanes are 300 nanometers (nm) in size and are composed of nanodomains of 20 nm in size with a γ -FeOOH struc-

ture. Each ferroxane particle is composed of a lepidocrocite core, on which AA is chemically adsorbed, as revealed by the spectroscopic techniques.

Thermolysis (cleavage of atomic bonds by exposure to high temperature) of the ferroxane-AA yields iron ceramic with the crystallographic structure of hematite. The specific surface area does not increase from the initial FeOOH mineral to the ferroxane-AA and the iron-ceramic, while the pore size distribution becomes monodisperse and the pore size diameter decreases from 55 to 12 and 13 nanometers after firing.

The ferroxane-AA was successfully doped with zirconium, which was

incorporated within the structure of the ferroxane-AA. After firing zirconium-doped ferroxane-AA samples, a mixed iron-zirconium oxide was formed.

Key to this work was the development of nanoparticles using a "green" chemistry approach. Also, the ferroxanes are indefinitely stable under ambient conditions and are adaptable to a wide range of processing techniques.

We are currently testing the possibility of using the ferroxanes for different applications such as the synthesis of iron membranes and the development of new catalytic materials.

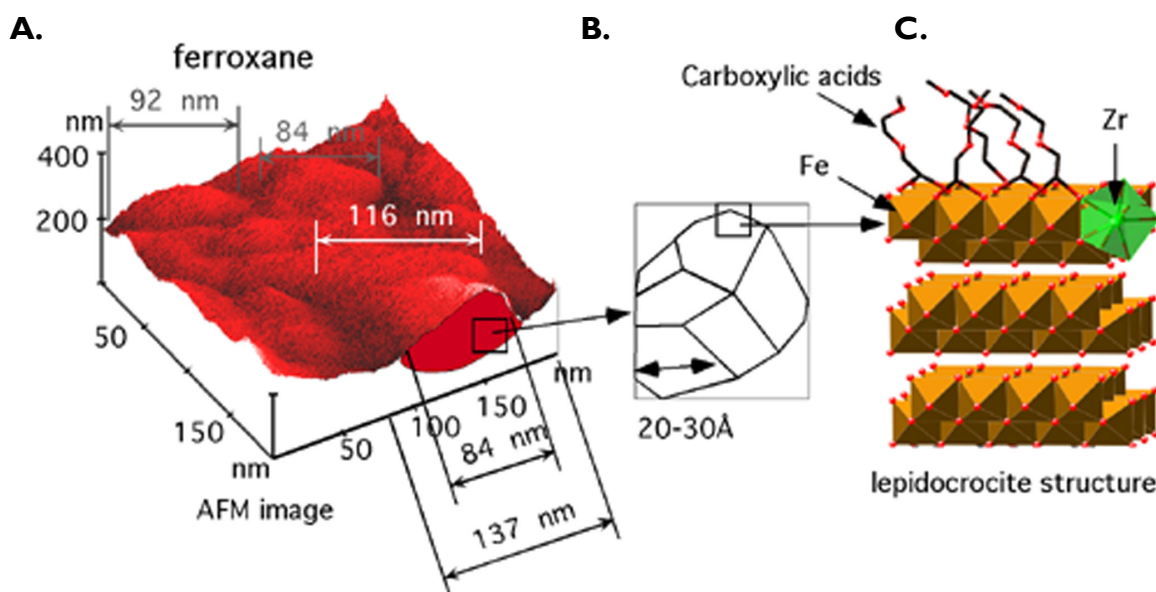


Figure1: (A) Atomic force microscopy (AFM) image of the texture and structure of ferroxane nanoparticles on a metallic surface. Apparent sizes of four ferroxanes are shown (116, 84, 92, and 84 nanometers). (B) Size of the nanodomains of each ferroxane. (C) Atomic structure of the nanodomains (brown: iron octahedra; red: oxygen atoms; green: zirconium site for doped sample).